Characterization of Photoelectrochemical Properties of SiC as a Water Splitting Material

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Abstract. Hydrogen attracts attention as an eco-friendly energy resource. The water splitting by semiconductor materials can generate hydrogen without CO_2 emission. However, the hydrogen conversion efficiency using conventional materials is not high enough, or the materials corrode easily. On the other hand, silicon carbide (SiC) is expected to be a water splitting material showing high conversion efficiency without corrosion. In this study, we characterized band edge potentials for 4H-, 6H- and 3C-SiC, and we revealed that they are capable of water splitting. We also estimated conversion efficiencies by photocurrent measurements in electrolytes for bulk 4H- and 6H-SiC.

Introduction

Hydrogen attracts attention as an eco-friendly energy resource. However, hydrogen is usually produced from the fossil fuel, and, in this production, a green house gas, CO_2, is also generated. The water splitting by solar light illumination to semiconductor materials can generate hydrogen without CO_2 emission. The conversion efficiency or durability of this method is not high enough for practical use. For example, metal oxides are conventional water splitting materials without corrosion in electrolytes. However, because they have wide band gap, the conversion efficiencies for these materials are only up to 1-2%. On the other hand, semiconductor materials other than metal oxides sometimes show high conversion efficiencies, but they are weak against corrosion. Thus, new water splitting materials, such as GaN, have been studied to obtain both high conversion efficiency and resistance to corrosion [1]. In general, a water splitting semiconductor material should meet three criteria: appropriate bandgap (1.6-2.2eV), good material durability and band edges straddling H_2O redox potentials. Silicon carbide (SiC) is chemically stable and can be made p-type with high crystal quality. P-type materials are generally more stable than n-type materials for water splitting, and thus p-type SiC could also be resistant to corrosion. Because of the wide band gap (> 2.9 eV), theoretical efficiencies reported in ref.2 for 4H- and 6H-SiC are not so high, ~1% and 2%. However, that for 3C-SiC is 8% because it has a band gap of 2.2 eV and can absorb visible light. Although many studies about electrochemical properties of SiC have been reported so far [3-6], reports on SiC as a water splitting material has been rarely found [6,7]. In this study, the photoelectrochemical properties of both n- and p-type SiC as a water splitting material were characterized and the conversion efficiencies were also estimated.

Experiment

Samples employed in this study were bulk grown n- and p-type 4H-and 6H-SiC along with n-type 3C-SiC. The thickness and resistivity of the samples are listed in Table 1. We fabricated ohmic contacts on the backside of the samples. Then the samples were fixed by silicone resin on polycarbonate plates with only the sample surface exposed. A wire was bonded on the ohmic contact and connected to a potentiostat so that the sample acted as the working electrode in the three electrode cell. Pt was used as a counter electrode, and a saturated calomel electrode (SCE) was used as a reference electrode.

Current-voltage (*I-V*) characteristics were measured under dark and light conditions. The electrolyte was a 0.5mol/l Na_2SO_4 aqueous soliution and the light source is a solar simulator whose power is 780 mW/cm^2. Band edge potential was estimated by the capacitance-voltage (*C-V*)

measurement with a measurement frequency of 1 kHz in electrolytes. As electrolytes, aqueous solutions with HCl (pH 1.5), Na_2SO_4 (pH 7) and NH_4OH (pH12.2) were employed. Time dependence of photocurrent under illumination by the solar simulator was measured in a 1mol/l H_2SO_4 aqueous solution with a potential of 0 V vs SCE. All the experiments were done at room temperature.

Results and discussion

Figure 1 shows *I-V* characteristics for n-type 4H-SiC. In the dark condition, current was observed at negative potentials vs SCE, and rectifying characteristics were observed. Under light illumitnation, photocurernt is observed at 0 V and positive potentials vs SCE. Figure 2 shows *I-V* characteristics for p-type 4H-SiC. Rectifying characteristics were observed and polarity was opposite to that for n-type 4H-SiC. If we illuminate an n-type SiC in electrolyte, it will be oxidized because of photogenerated hole react with H_2O in electrolyte as shown in inset of Fig.1. On the other hand, in the case of p-type SiC, photogenerated electron react with H^+ ions as shown in inset of Fig.2. As shown in Fig.2, photocurrent from p-type 4H-SiC was observed under illumination below 0.5 V vs SCE. For 6H-SiC, similar results were obtained. In contrast, n-type 3C-SiC showed rectifying characteristics but little photocurrent at 0 V vs SCE under light illumination. Figure 3 shows a Mott-Schottky plot for n-type 4H-SiC. In this plot, the intercept with the x-axis corresponds to a flat band potential, V_{fb}. For this sample $V_{fb} = -1.84$ V. Using V_{fb} and the Fermi level estimated from donor or acceptor concentrations, we obtained the band edge potentials in various pH for the samples as shown in Fig.4. The band edge potential for p-type 6H-SiC is not shown in this figure because the *C-V* measurement was not able to be performed for this sample due to high resistivity. In this figure, we also show the redox potentials of H^+ / H_2 and O_2 / H_2O as the top and bottom of the gray band. If the edge of the conduction band is located above the redox potential of H^+ / H^2 and the edge of valence band is located below the redox potential of O_2 / H_2O, the water splitting is possible. The conduction band edge of 3C-SiC is near to the redox potential of H^+ / H_2, while other polytypes clearly have band edge potentials capable of the water splitting in all pH. Although, in principle, the band edge potential does not depend on the conduction type, the estimated band edge potential for n-type 4H-SiC is 1 eV above that of p-type 4H-SiC. This reason is still unclear and further investigation for the band edge potential is required.

Table 1 Thickness and resistivity of the samples

	n-4H	p-4H	n-6H	p-6H	n-3C
Thickness (μm)	350	346	260	400	303
Resistivity (Ωcm)	0.01-0.05	500-2500	0.1	1.5×10^{7}-1.0×10^{12}	1.0
Doping density (cm^{-3})	1×10^{19}	2×10^{17}	4×10^{19}	-	2×10^{19}

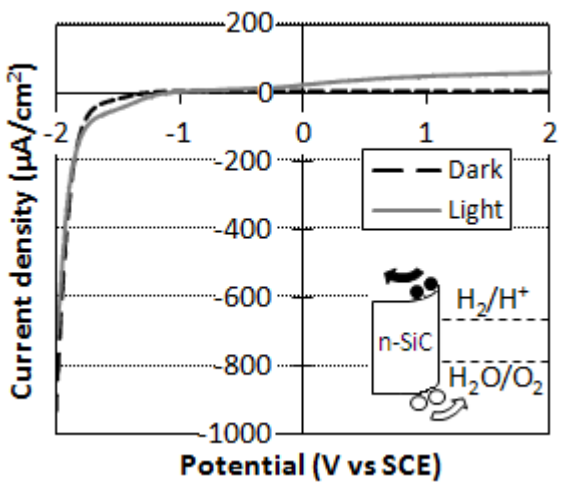

Fig. 1 *I-V* characteristics in a 0.5mol/l Na_2SO_4 aqueous soliution for n-type 4H-SiC. An insert is schematic of water splitting for n-type samples.

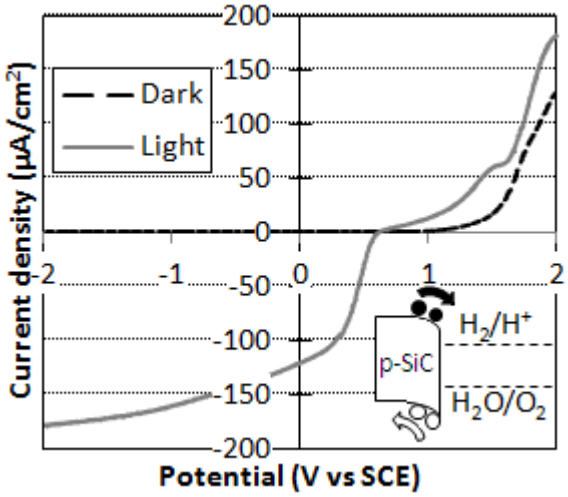

Fig. 2 *I-V* characteristics in a 0.5mol/l Na_2SO_4 aqueous soliution for p-type 4H-SiC. An insert is schematic of water splitting for p-type samples.

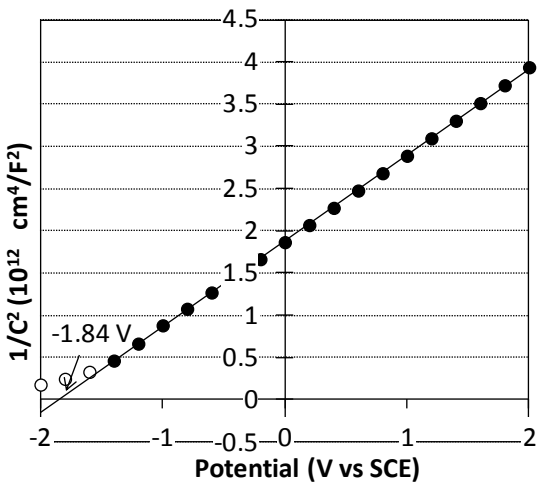

Fig. 3 Mott-schottky plot for n-type 4H-SiC in pH 7 (0.5mol/l Na_2SO_4 aqueous soliution). The intercept with the x-axis corresponds to the flat band potential.

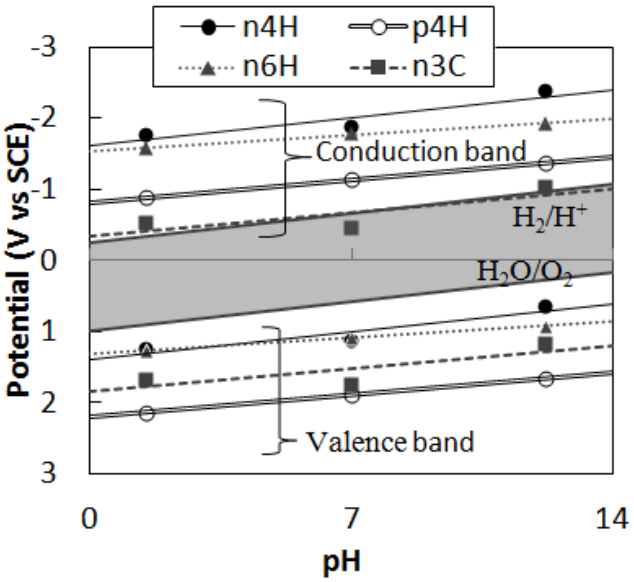

Fig. 4 Band edge potential of SiC in various pH. The redox potentials of H^+/H and of O_2/H_2O are also indicated by the top and bottom lines of the gray band.

Figure 5 shows the time dependence of photocurrents under light illumination for the n-type samples. In all the n-type samples, the photocurrents are very small and decrease gradually. Figure 6 shows photocurrents for the p-type samples. The photocurrents are larger than those for the n-type samples and do not significantly decrease with time. Small steps observed in photocurrent for the p-type 4H-SiC may be due to instability of light source. We calculated the conversion efficiency η from

$$\eta\ (\%) = \frac{I \times 1.23}{L} \times 100 \qquad (1)$$

where I is the photocurrent, L is the light intensity, and 1.23 means the redox potential width between H^+ / H_2 and O_2 / H_2O. Table 2 lists obtained conversion efficiencies for the samples. In this estimation, we use stable photocurrents after the initial reduction for the n-type samples. The conversion efficiency for n-type 3C-SiC is not shown due to its very small photocurrent. The efficiencies for the n-type samples are much lower than those for the p-type samples. It is known that SiC is oxidized by light illumination in an electrolyte [7], and resulting SiO_2 behaves as a resistant layer for photocurrent. Therefore, the small and decreasing photocurrent for the n-type samples would be caused by SiO_2 formation. Among all the samples, the highest conversion efficiency of 0.024% is obtained for p-type 4H-SiC.

We confirmed no corrosion for the p-type samples after the measurements of photocurrent by an optical microscope and a profilometer observation, and thus p-type SiC is promising for water splitting application. We should note that the efficiencies obtained in this study are calculated from photocurrent and not from measured volume of H_2. In addition, photocurrent was measured by the three electrodes system with the potential adjusted at 0 V vs SCE. If we use a two electrode system, the conversion efficiency may be different. In addition, the samples employed in this study were bulk ones, and thus carrier lifetimes should be short and doping densities are relatively high. These factor have negative influence on the efficiency. We are now trying to characterize epitaxial samples to improve efficiencies. The epitaxial samples have higher crystalline quality than the bulk samples and are expected to show higher efficiencies.Results for the epitaxial samples will be reported elsewhere.

Table 2 Conversion efficiencies estimated from photocurrent

Conduction type	4H	6H
n	6.3×10^{-5} %	4.7×10^{-5} %
p	0.024 %	0.011 %

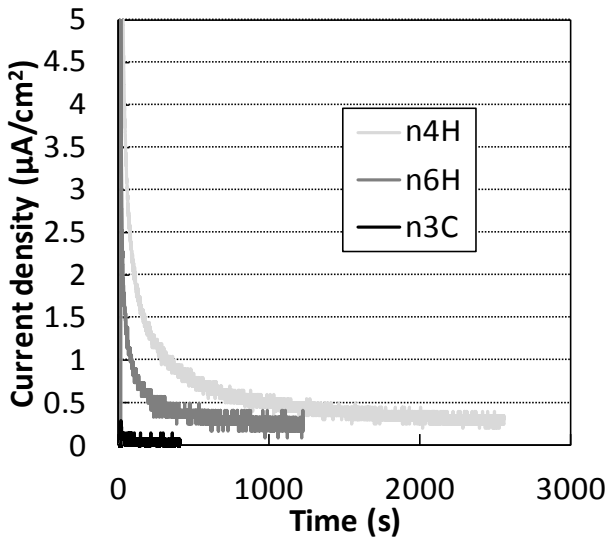

Fig. 5 Time dependence of photocurrent for the n-type samples.

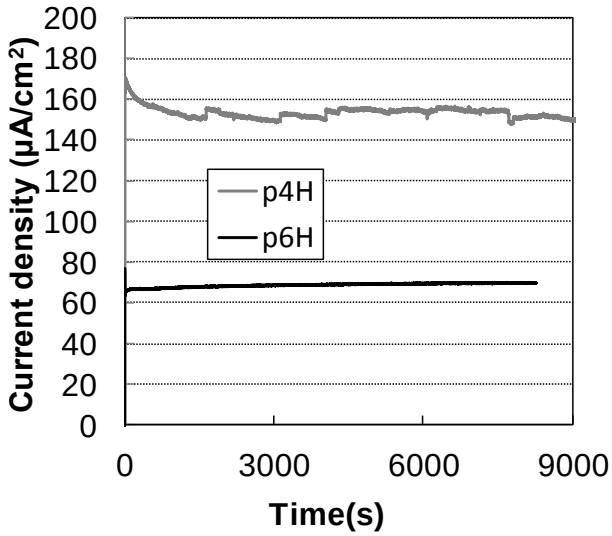

Fig. 6 Time dependence of photocurrent for the p-type samples.

Conclusions

We characterized photoelectrochemical properties of SiC as a water splitting material. Band edge potentials were estimated from *C-V* measurements for 4H-, 6H-SiC and 3C-SiC, and all the polytypes seem to have band edge potentials capable of water splitting. From photocurrent under light illumination in electrolytes, the conversion efficiencies were estimated to be 0.024% and 0.011% for p-type 4H- and 6H-SiC, respectively, and p-type SiC did not corrode under illumination in the electrolytes. These results suggest that p-type SiC is promising as a water splitting material.

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